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MODIFICATIONS OF THE ACTIVATED SLUDGE PROCESS FOR NITRIFICATION AND DENITRIFICATION

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Federal Water Quality Administration
Cincinnati, Ohio

August 1970

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ABSTRACT

Several modifications of the activated sludge process incorporating single, dual and three sludge systems were evaluated for nitrification and denitrification in a 0.2 mgd pilot plant. Results indicate that the three sludge system provides the most dependable, consistent operation although it is slightly more expensive in capital costs. Preliminary results of nitrification and denitrification rate dependence upon temperature, design considerations, oxygen uptake rates, surface overflow rates, and solids production rates are presented and discussed.

Key words: activated sludge, nitrification, denitrification

MODIFICATIONS OF THE ACTIVATED SLUDGE PROCESS FOR NITRIFICATION AND DENITRIFICATION*

By

M. C. Mulbarger**

In a cooperative effort, Prince William County, Virginia and the Federal Water Quality Administration have evaluated several modifications of the activated sludge process for nitrification and denitrification in the 0.2 mgd (760 cu m/day) Manassas Pilot Plant (1). This manuscript reports the activities leading to the selection of the most optimum process sequence and cites preliminary observations of integrated system performance.

FACILITY

The 0.2 mgd (760 cu m/day) pilot plant represents a scale-up of the three sludge, biological-chemical nitrogen and phosphorus removal system proposed by Barth, et al. (2). The facility was built above ground, fully exposed to local climatic conditions, to obtain maximum applicability of the results. Its designed flexibility, through reactor compartmentalization and extra piping, allows any modification of the activated sludge process to be set into service. It operates in parallel with a larger municipal wastewater treatment facility and receives screened, shredded and degritted influent wastewater from a common wet well.

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TECHNIQUES

Valid measurements of biological system performance entail the use of a conditioning period prior to process evaluation of about two to three times the operating cell residence time (3), which is defined as the pounds of solids under aeration divided by the pounds of solids lost in the effluent and wasted per day. Any conditioning period less then this results in merely indicative measurements of process performance with a confidence value equivalent to the equilibrium value utilized. System equilibrium values (degree of approach to steady state conditions) prior to the investigative period are presented in this paper.

Aerator dissolved oxygen values were determined by a lead-silver electrode. Brucine nitrate nitrogen determinations and all other analytical procedures followed Standard Methods (4). Soluble wastewater constituents are defined as those which pass through a Whatman No. 5 filter.

Each of the reported studies was performed at nearly constant flow. Samples were collected every two hours, composited and analyzed daily. Sampling times in the seven-day studies were staggered to simulate a 24-hour plug flow of wastewater through the plant. Sampling times were not staggered in longer investigative periods.

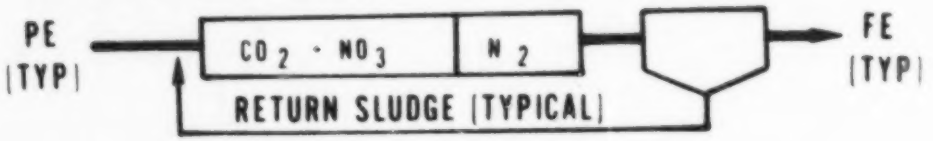
PROCESS ALTERNATIVES

Figure 1 shows several feasible activated sludge process modifications for nitrification and denitrification. Other potential process alternatives would include substituting trickling filtration for the high rate and/or nitrifying activated sludge systems (5), adding inorganic or organic coagulants to the primary clarifier to maximize solids removal and eliminate

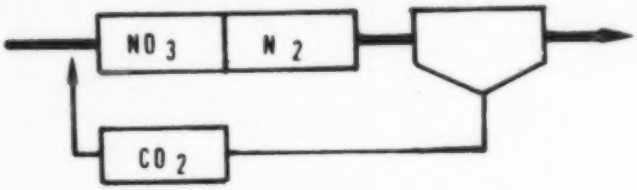
FIGURE 1
PROCESS ALTERNATIVES FOR NITRIFICATION - DENITRIFICATION

I SINGLE SLUDGE SYSTEMS

A. EXTENDED AERATION

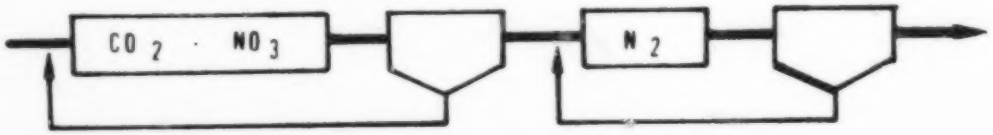


B. CONTACT STABILIZATION MODIFICATION

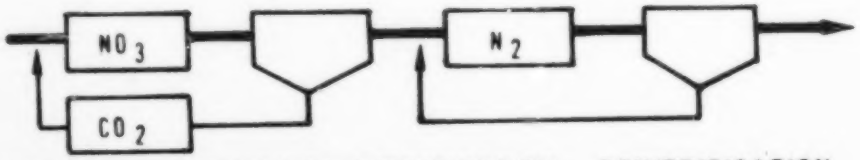


II DUAL SLUDGE SYSTEMS

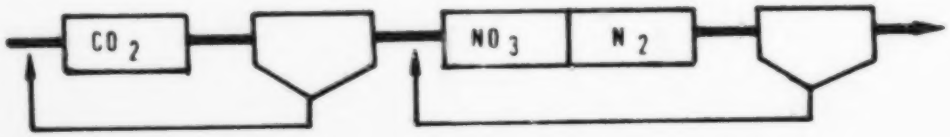
A. EXTENDED AERATION WITH ISOLATED DENITRIFICATION



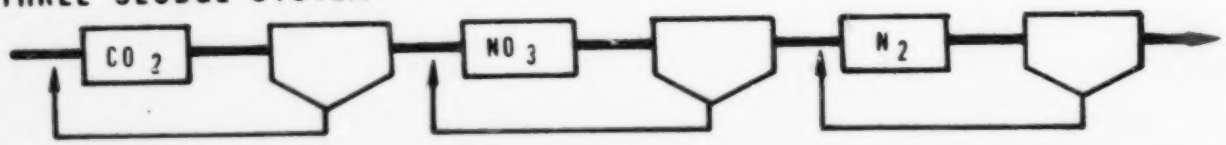
B. CONTACT STABILIZATION MODIFICATION WITH ISOLATED DENITRIFICATION



C. HIGH RATE WITH COMBINED NITRIFICATION - DENITRIFICATION



III. THREE SLUDGE SYSTEM



CODE

CO_2 CARBON REMOVAL OXIDATION - SYNTHESIS

NO_3 NITRIFICATION

N_2 - DENITRIFICATION

the high rate activated sludge system, and utilizing anaerobic columns or beds for denitrification (6).

Process alternatives IB (single sludge), IIB and IIC (dual sludge), and III (three sludge) were evaluated in the Manassas Pilot Plant. Extended aeration systems were not evaluated since it was felt that contact stabilization modifications would achieve similar results and be economically superior. Performance of alternative IIA, through nitrification, and detailed investigations with nitrification can be found in the publications of Downing and his co-investigators (7)(8)(9)(10)(11).

EVALUATION

Figures 2 and 3 and Table I summarize nitrification and denitrification performance as a function of the system or process alternative. Nitrification performance is represented by Total Kjeldahl Nitrogen (TKN) removal or oxidation since it includes both organic and ammonia nitrogen and results obtained from this analytical procedure are not as variable as those encountered with nitrate determinations. Nitrogen removal in the denitrification system was separated into synthesis and denitrification fractions by mass balance techniques. The results were obtained from seven-day investigations which were conducted from November through April.

Essentially constant soluble effluent TKN values were measured from the isolated nitrification system (Figure 2) once an appropriate combination of hydraulic contact time and mixed liquor volatile suspended solids (MLVSS) was established. A combined nitrification system (Figure 3) failed to exhibit the same degree of soluble effluent TKN stability at similar MLVSS concentrations and hydraulic detention times. The isolated nitrification

FIGURE 2
PERFORMANCE OF ISOLATED NITRIFICATION SYSTEM

SYSTEM	III			
EQUILIBRIUM FRACTION PRIOR TO STUDY INITIATION	0 99·	0 99·	0 99·	0 74
CELL RESIDENCE TIME DAYS	13	10	17	11
AERATION DETENTION TIME HRS	3 0	2 7	3 7	2 8
LIQUID TEMP C	13 5	12 0	11 0	11 5
DISSOLVED OXYGEN mg l	5 2	2 9	3 9	2 8
MLVSS mg l	1190	1430	1970	2300
SOLUBLE EFFLUENT COD mg l	26	27	24	28

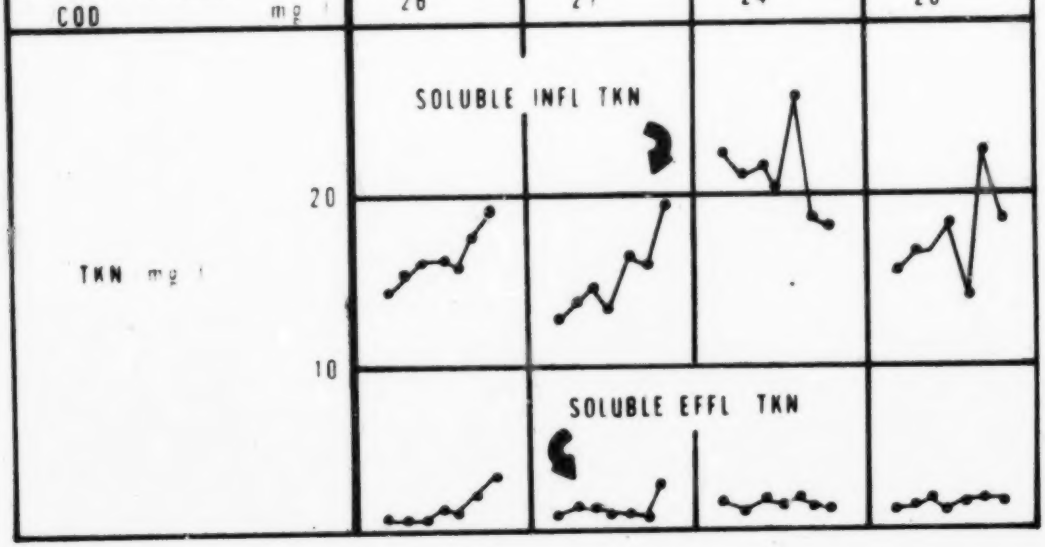


FIGURE 3
PERFORMANCE OF COMBINED NITRIFICATION SYSTEM

SYSTEM	II B			I B	
EQUILIBRIUM FRACTION PRIOR TO STUDY INITIATION	0 95	0 99	0 20	0 78	0 85
CELL RESIDENCE TIME DAYS	9	11	65	30	15
AERATION DETENTION TIME HRS	1 0	1 5	2 6	2 2	3 1
REAERATION DETENTION TIME HRS	9 6	7 0	5 0	5 4	2 5
LIQUID TEMP C	19	15 5	12 5	12 5	13 5
DISSOLVED OXYGEN mg l	4 7	3 9	4 6	4 2	3 5
MLVSS mg l	500	2810	1570	2140	2390
SOLUBLE EFFLUENT COD mg l	55	37	30	34	39

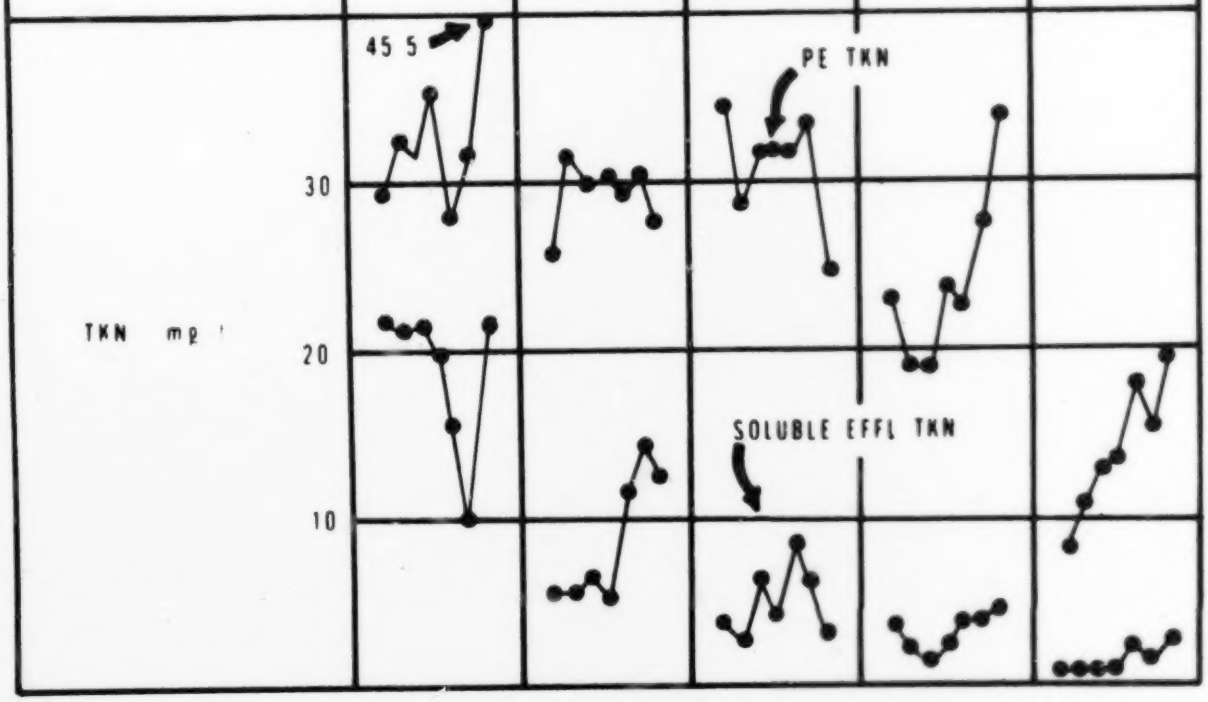


TABLE 1-DENITRIFCATION SYSTEM PERFORMANCE

ITEM	SYSTEM	III		IIB	IIC	IB
		THREE SLUDGE		DUAL	SLUDGE	SINGLE SLUDGE
	ADDITION	METHANOL	METHANOL 50% WASTE HIGH RATE ACT SL	METHANOL	METHANOL	METHANOL
Equilibrium Fraction Prior to Study Initiation		0 99+	0 76	0 94	0 66	0 85
Liquid Temperature	C	10	11 5	11 5	9 5	13 5
Cell Residence Time	Days	7 6	5 2	5 0	7 5	15
MLVSS	mg l	2460	2350	2400	2333	2390
System Influent						
Soluble TKN	mg l	0 8	1 1	4 9	12 1	13 8
NO_3 N	mg l	17 9	19 5	12 1	0 7	0 9
System Effluent						
Soluble TKN	mg l	0 9	1 1	2 8	0 9	1 0
NO_2 N	mg l	TR	0 2	TR	0 6	TR
NO_3 N	mg l	0 7	5 0	1 2	1 2	1 4
Soluble COD	mg l	22	26	22	34	39
METHANOL ADDED	mg/l	55	37	35	52	49
Nitrogen Removals — Lb N Removed / Lb Soluble COD Removed						
Due to Synthesis		0 02	0 03	0 03	< 0 01	0 03
Due to Denitrification		0 23	0 24	0 22	0 13	0 10
Total Removal		0 25	0 27	0 25	0 13	0 13

system also consistently produced lower soluble effluent CODs than measured in the combined systems. Table I shows substantially better COD usage (pounds of nitrogen removed per pound of soluble COD removed where the soluble COD removed is the influent plus methanol COD minus the effluent COD) and lower soluble effluent CODs when operating with an isolated denitrification system, systems III and IIB. A minimal gain in nitrogen removal capability was obtained by combining methanol additions with waste activated sludge.

From these studies the conclusion was reached that while nitrification and denitrification could be achieved and maintained in any of the process alternatives investigated, the three sludge system provided optimum dependable and consistent performance. Its superior performance for carbon removal, nitrification, and denitrification is directly attributable to the use of isolated, optimized sludge cultures. Mixing carbon removal with nitrification not only results in a loss of soluble carbon removal efficiency but necessitates a longer aeration time for nitrification. This is due not only to a loss of an optimized sludge culture but also to a loss of nitrogen removal due to sludge synthesis which, in a high-rate activated sludge system, removes 20 to 40 percent of the nitrogen before it is applied to the nitrification system.

Even though preliminary capital cost estimates (Table 2) show it to be the most expensive of the alternatives investigated, the three sludge system was selected for long-term evaluation because of its performance consistency, operational simplicity, buffering capability and superior compatability with metal salt additions for phosphorus removal (3). These cost estimates also show that nitrification can be provided at a cost

TABLE 2 - CAPITAL COST COMPARISON - 10 mgd BASIS
(In Millions of 1969-70 Dollars)

ITEM \ SYSTEM	STD. RATE A.S. PLANT	IA	IB	IIA	IIB	IIC	III
Pretreatment, Control Building, Primary and Final Clarification, and Disinfection	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Sludge Thickening, Dewatering, Treatment and Disposal	2.6	2.2	2.2	2.2	2.2	3.0	3.0
Aeration	1.1 - 1.4					0.3 - 0.5	0.3- 0.5
	5.2 - 5.5					4.8 - 5.0	4.8-5.0
Nitrification		1.9 - 2.7	1.1 - 1.5	1.9 - 2.7	1.1 - 1.5	0.9 - 1.1	0.9 - 1.1
				5.6 - 6.4	4.8 - 5.2		5.7 - 6.1
Denitrification		0.5 - 0.7	0.5 - 0.7	0.9 - 1.1	0.9 - 1.1	0.5 - 0.7	0.9 - 1.1
		6.1 - 7.1	5.3 - 5.9	6.5 - 7.5	5.7 - 6.3	6.2 - 6.8	6.6 - 7.2

within plus or minus ten percent of the cost of conventional activated cludge treatment.

PROCESS PERFORMANCE

Figure 4 is a time-dependent nitrogen profile through the three sludge system; all measurements after the influent and primary effluent are for soluble nitrogen forms. This figure indicates that incomplete organic nitrogen hydrolysis to ammonia occurs in the high-rate activated sludge system, complete nitrogen oxidation is achieved after two hours in the nitrifying activated sludge system, denitrification proceeds rapidly to a point controlled by the methanol dose, and intermediate nitrite formed during denitrification is oxidized back to nitrate nitrogen in the aeration channel. With proper methanol addition, all of the nitrogen except an apparent nonbiodegradable residual would have been removed.

Average performance of the three sludge system over two seventeen-day studies is summarized in Table 3. The pilot plant received an average flow of 0.23 mgd (870 cu m/day) which resulted in surface overflow rates in the primary, first-stage, second-stage, and final clarifiers of 1150, 1200, 1280 and 750 gpd/ft^2 (47, 49, 52 and 30 cu m/day/sq m). The average methanol dose was 40 mg/l and the high-rate activated sludge system received an average sodium aluminate dose of 14.3 mg/l as Al^{+3}. A polishing dose of 2.2 mg/l as Al^{+3} was applied to the aerated channel in only one 17-day study; thus, final effluent phosphorus values are not subject to direct interpretation. Investigations concerning combined biological-chemical phosphorus removal can be found elsewhere (3). Ammonia breakthrough is due to the appearance of toxic compounds in the wastewater (see later) and an operator's error.

FIGURE 4

NITROGEN TRANSFORMATIONS THROUGH THREE SLUDGE SYSTEMS

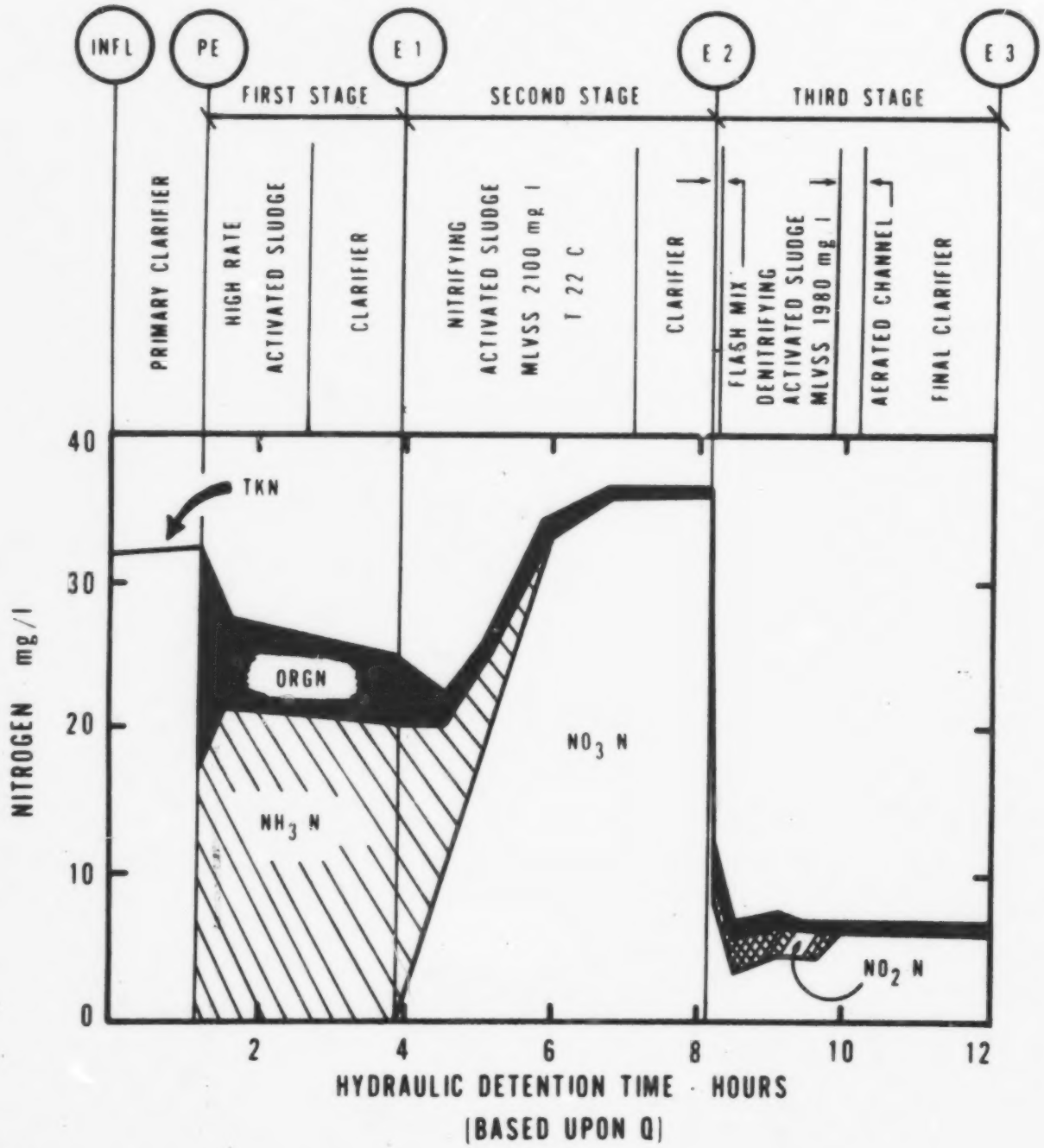


TABLE 3 - THREE SLUDGE SYSTEM PERFORMANCE

ITEM** - mg/l		INFL	PE	E-1	E-2	E-3
SS		137	86	39	18	27
COD		314	217	70	34	35
COD*		-	-	43	19	20
P		13.7	12.4	4.6	3.8	3.5
P*		-	-	2.9	2.9	2.4
TKN		25.2	25.8	21.8	6.3	5.4
NH_3-N				-	2.2	1.4
NO_2-N		-	-	TR	TR	0.4
NO_3-N		-	-	TR	14.6	3.5
BOD_5/COD	Average Result of 15 Measurements	0.40	0.46	0.22	0.41	0.26
BOD_5^*/COD^*		-	-	0.15	0.05	0.06

* Soluble Analyses

** See Figure 4

PROCESS DESIGN

Firm design and operational recommendations cannot be made at this time. The discussion in this section is limited to a three sludge system receiving sodium aluminate for phosphorus removal and reports only preliminary observations and measurements. The reader should remember that sludge systems unavoidably mix due to floc carry over (effluent suspended solids) and true, long-term equilibrium values were rarely measured because of the many process alternatives studied. Mixed liquor volatile suspended solids measurements as determined by Standard Methods (4) are utilized for consistency unless otherwise noted; however, this procedure gives a fictitiuosly high valuc in a combined chemical-biological system due to the loss of chemically bound water. Incorporating an acid pretreatment procedure (12) before conventional ashing of the sample in the two 17-day studies reduced the measured volatile fraction of the mixed liquor suspended solids in the nitrification and denitrification systems from 54 to 45 percent.

HIGH-RATE ACTIVATED SLUDGE SYSTEM

The first-stage high-rate activated sludge system has been satisfactorily operated with an aeration detention time of 1.5 hours and a cell residence time of 2 $\pm$ 1 days. Background measurements show a net volatile solids production of about 0.39 pounds of volatile solids produced per pound of COD removed. The addition of approximately 14 mg/l of sodium aluminate (as Al^{+3}) results in a Sludge Volume Index of 40 to 50 and an additional solids production of about 55 mg/l. Sludge settling studies to determine the unhindered settling velocity of the sludge interface

indicate that a surface overflow rate of 1640 ± 240 gpd/ft^2 (67 ± 10 cu m/day/sq m) can be safely handled. Reducing the aeration detention time and/or cell residence times to less than one hour and one day, respectively, results in a poorer settling sludge. Capability should be provided to waste solids from this system to both the nitrifying and denitrifying activated sludge systems.

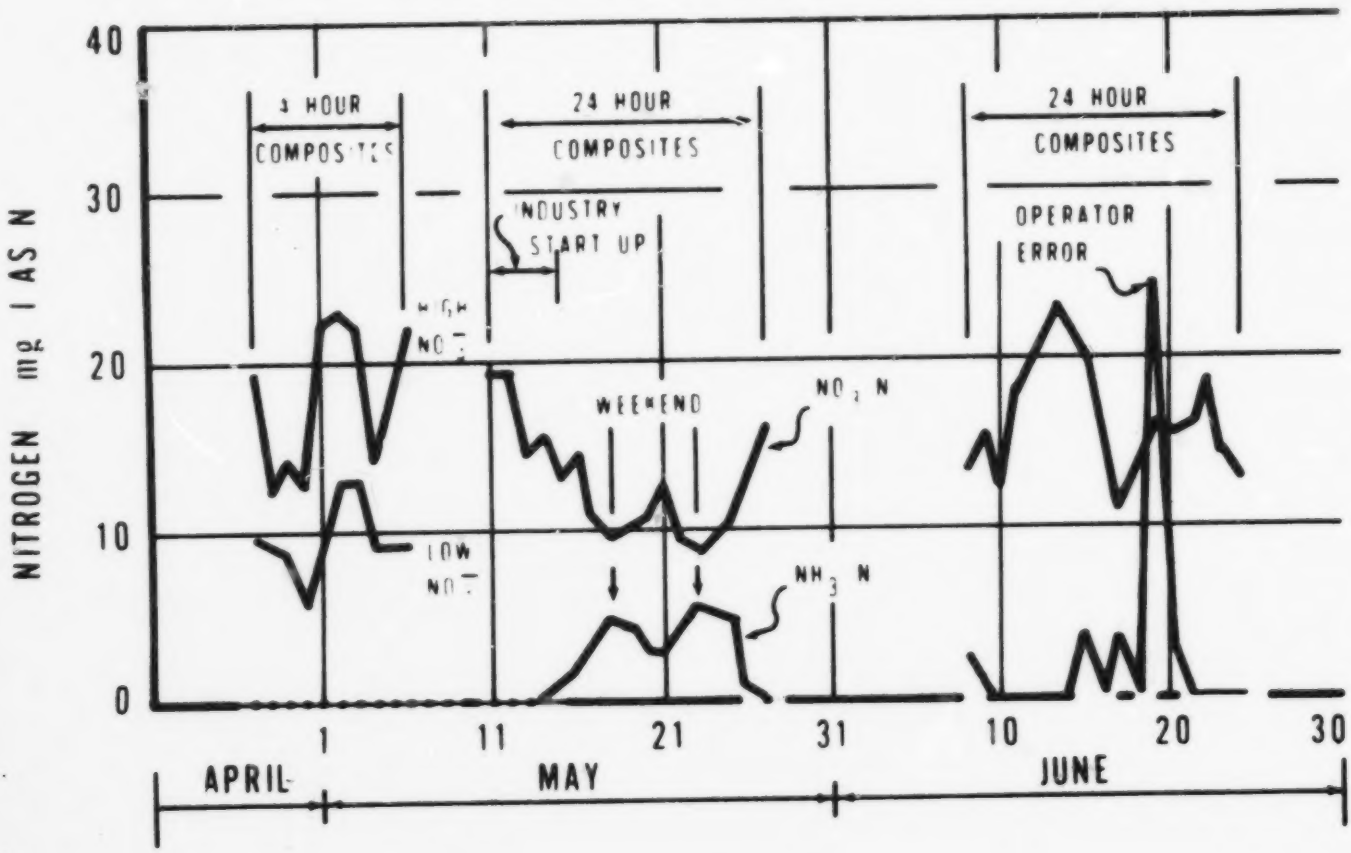
NITRIFICATION ACTIVATED SLUDGE SYSTEM

The nitrification system is operated at a cell residence time of 10 to 15 days with an aeration detention time of 2.5 to 3.0 hours. Future variable flow studies will incorporate a detention time of 3.5 to 4.0 hours at nominal flows and provide 2.5 hours at peak flow conditions. Solids wastage from this system is dictated more by the effluent suspended solids from the high-rate activated sludge system than actual solids production. Studies to date have indicated only minimal solids growth, ranging from a net loss to a production of about 0.10 pounds of nonacid-soluble volatile solids per pound of soluble COD removed. Sludge settling rates from the system indicate that a surface overflow rate of 1320 ± 300 gpd/ft^2 (54 ± 12 cu m/day sq m) could be utilized. Sludge volume indices typically range from 50 to 80.

Toxicity is a paramount concern with nitrifying organisms (8). Nitrification inhibition has coincided with the startup of a new industry in Manassas. Figure 5 shows the ammonia and nitrate nitrogen concentration in the nitrification system's effluent before and after the industry began discharging to the sanitary sewer. Ten days of four-hour composites preceded the industry's startup, during this time no ammonia breakthrough occurred.

FIGURE 5

NITRIFICATION TOXICITY

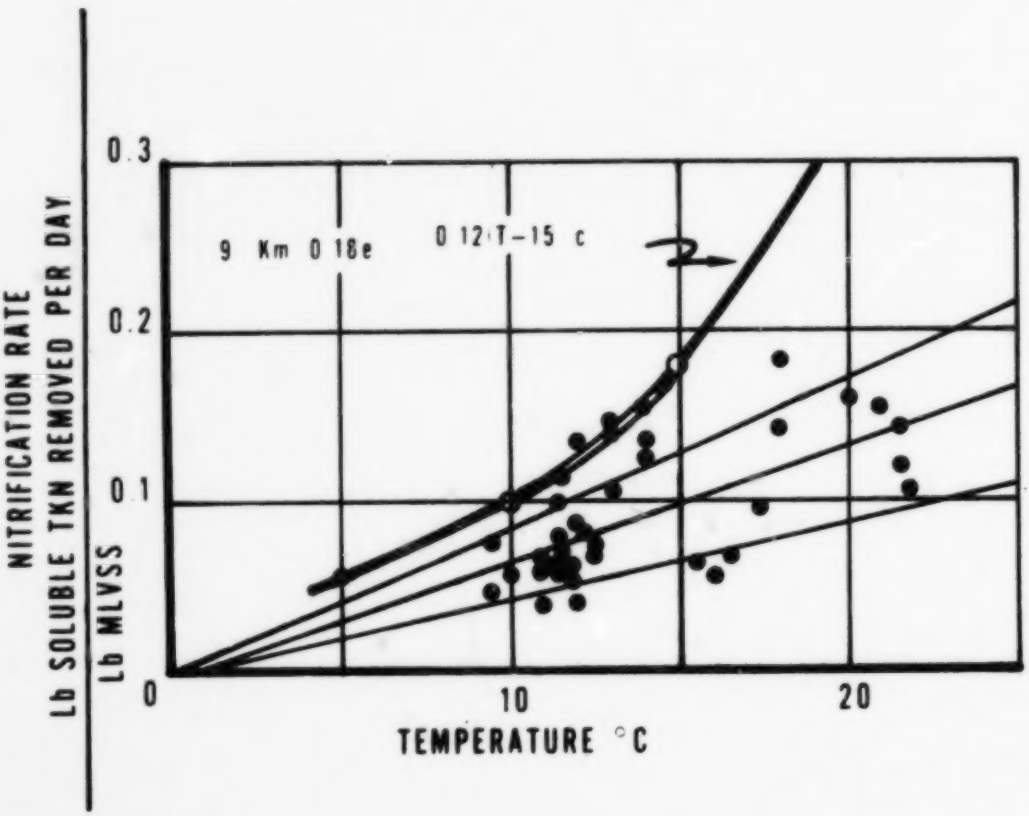


After startup, weekend nitrification inhibition followed by recovery during the week was noted. A later seventeen-day study showed that the system was still affected by these slug discharges but not to the same extent as previously observed in the original seventeen-day study. The causative agent or agents have yet to be isolated. The high ammonia breakthrough on June 19 was due to an operator's error which resulted in the volumetric displacement of the main plant's primary anaerobic digester to the wet well and hence to the pilot plant over an eight-hour period.

Nitrification in an inadequately buffered wastewater may cause a pH depression. pH depression due to nitrification may, in turn, attenuate nitrification performance since nitrification optimally proceeds at a pH about 8 (7). Theoretically, an alkalinity depletion of 7.1 pounds of $CaCO_3$ per pound of nitrate nitrogen produced would be predicted; the average value found for 69 investigative days was 6.1 pounds $CaCO_3$/pound NO_3-N. It can be concluded that the alkalinity depletion due to nitrification will be less than the theoretical prediction but, in low alkaline wastewaters, it may be of sufficient magnitude to necessitate the addition of external sources of alkalinity for pH control.

Figure 6 shows the dependence of the nitrification rate on liquid temperature. The data points were obtained by time dependent nitrogen profiles through the nitrification system. The performance envelope was obtained by determining the mean $\pm$ standard deviation of the data points between 10 and 12.5°C and between 20 and 22.5°C. pH values in the low temperature range were between 7.1 and 7.3 and in the high temperature range between 7.7 and 7.9.

FIGURE 6 - NITRIFICATION RATE VS. TEMPERATURE



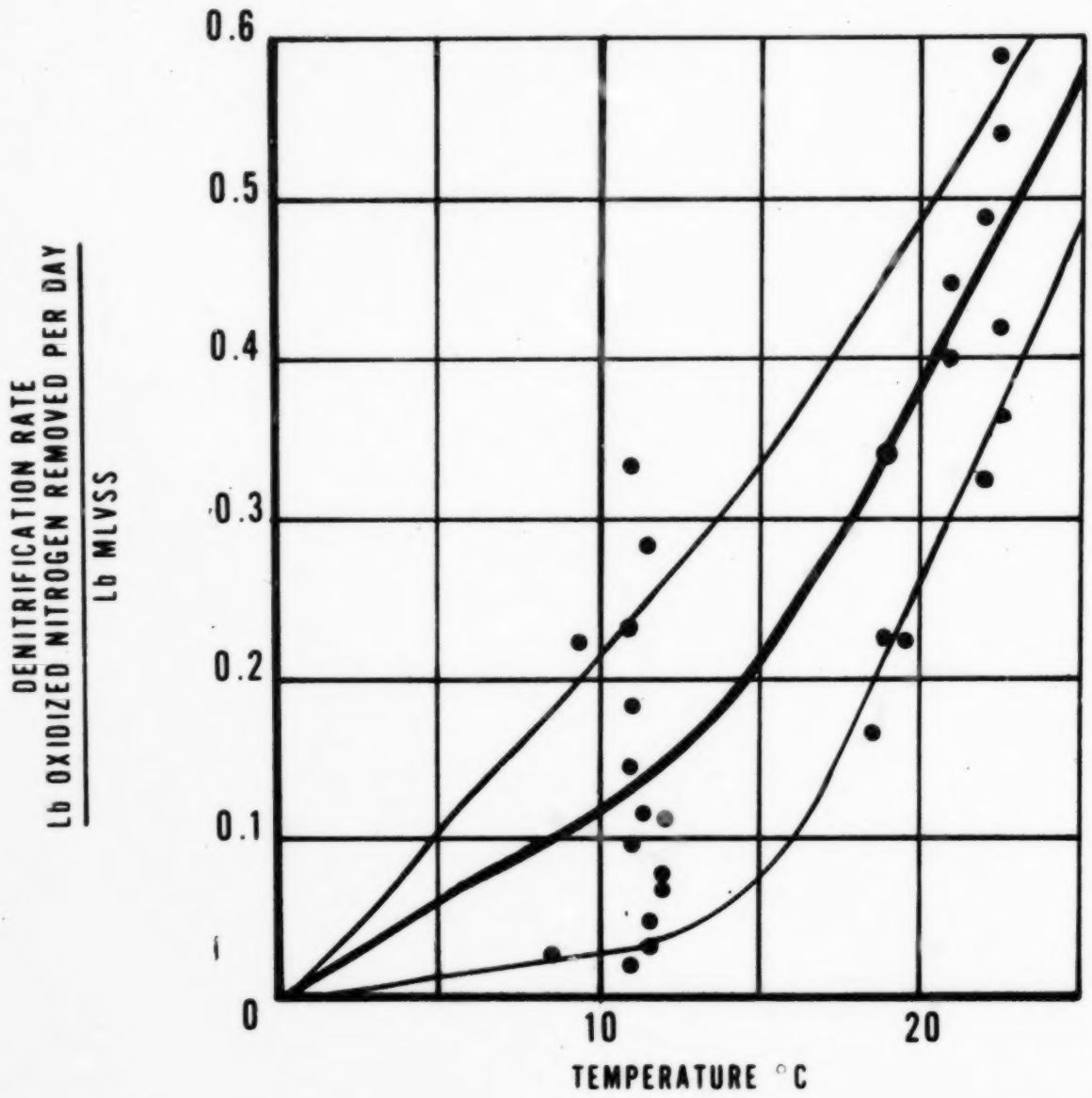
Assuming the theoretical oxygen requirement for ammonia oxidation (4.57 pounds of oxygen per pound of ammonia nitrogen), the nitrification rate measured at 20°C would be equivalent to an oxygen uptake rate of 25 ± 9 mg O_2/HR/gm MLVSS which closely corresponds to a measured oxygen uptake rate of 20 ± 10 mg O_2/HR/gm MLVSS at a temperature of 20 ± 1°C.

Since the rate of nitrification and the growth rate of Nitrosomonas should be equivalent, a reported growth rate for Nitrosomonas (9) is also shown on Figure 6 for comparison. The operating cell residence time for nitrification must be equal to or greater than the reciprocal of the growth or nitrification rate. Failure to achieve the reported first-order relationship may be due to the fact that high temperature measurements were made during the period that the pilot plant was receiving periodic slug discharges of an inhibiting industrial waste. Nonacid-soluble volatile solids measurements would increase the reported reaction rate by about twenty percent and would have given closer agreement at lower reaction temperatures. Failure to have complete system equilibrium and unavoidable pH differences further account for the lack of agreement.

DENITRIFICATION ACTIVATED SLUDGE SYSTEM

The dependence of the denitrification rate upon temperature was measured using the same techniques incorporated in the nitrification studies. The denitrification rate shown in Figure 7 shows a nonlinear temperature variation. The faster rate of denitrification is attributed to the greater number of organisms that can perform the denitrification reaction. Oxygen uptake rates of 60 ± 30 mg O_2/HR/gm MLVSS at a temperature of 21 ± 1°C have been measured in this system. Assuming the theoretical requirement for denitrification (2.86 pounds of oxygen per pound of nitrate nitrogen),

FIGURE 7 · DENITRIFICATION RATE VS. TEMPERATURE



the measured denitrification rate at 21°C would correspond to an oxygen uptake rate of 81 ± 12 mg O_2/HR/gm MLVSS.

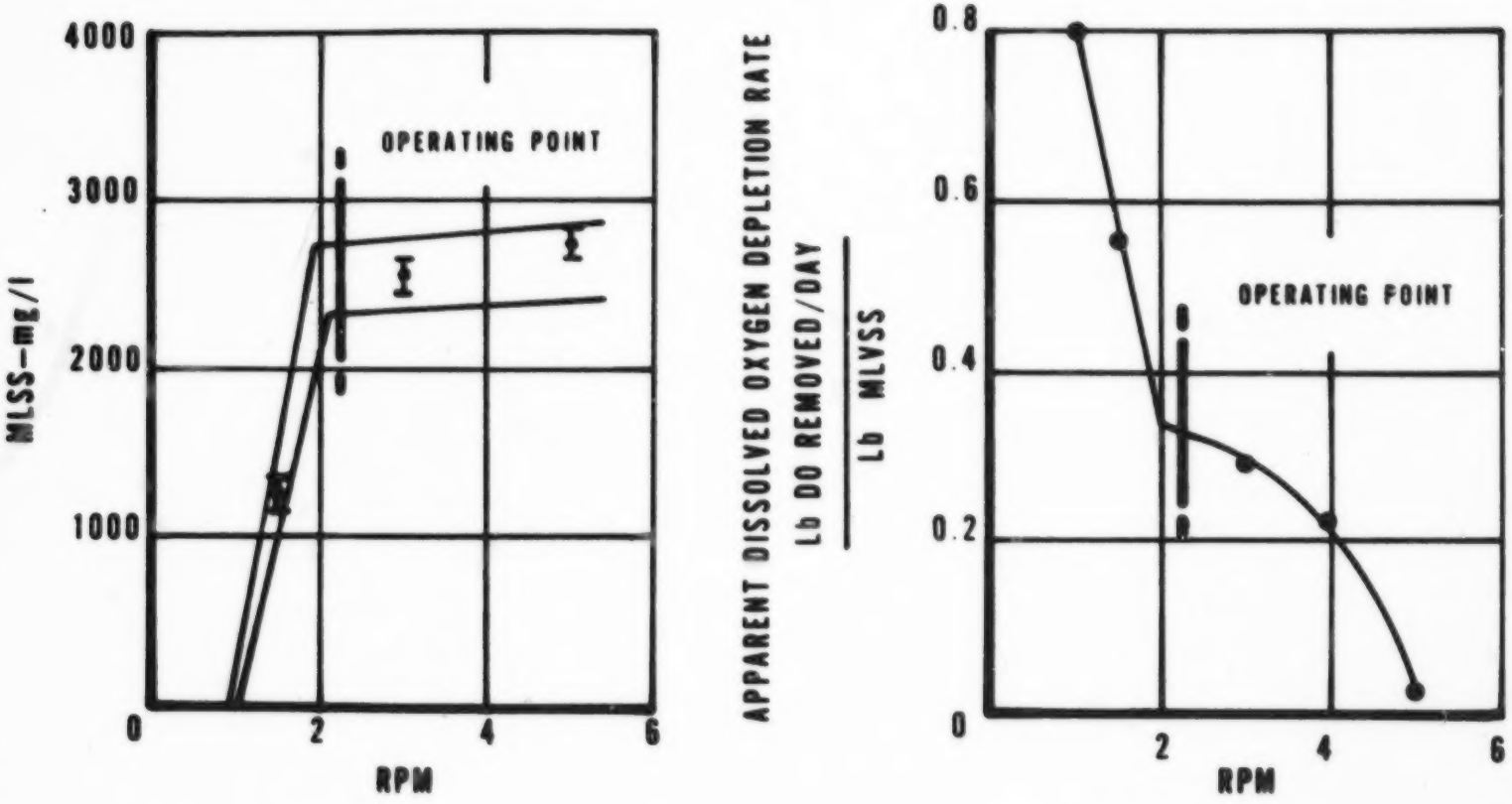
Sludge settling curves indicate that a surface overflow rate of 1620 ± 230 gpd/ft^2 (66 ± 9 cu m/day/sq m) would be satisfactory for solids-liquid separation; however, since this unit process represents the last treatment step, a more conservative design figure is indicated. The system's Sludge Volume Index varies between 40 and 60. The added methanol is preferentially oxidized rather than synthesized and volatile solids production figures typically range between 0.04 and 0.10 pounds of nonacid-soluble volatile solids produced per pound of soluble COD removed.

In the reported studies, a constant daily rate of methanol was added at the beginning of the open denitrification reactor. These additions were based upon historic plant performance and methanol requirements. The denitrification reaction goes directly to completion if enough methanol is added but gross overdosages can deteriorate effluent CODs. Methanol requirements are dictated by influent nitrate and dissolved oxygen concentrations, cellular synthesis and energy requirements, and the magnitude of oxygen transfer at the reactor's air/liquid interface. A methanol requirement of about 3 to 3.5 parts of methanol per part of nitrate nitrogen (24-hour composite) produced oxidized nitrogen concentrations in the effluent of less than 2 mg/l. Possibly, sealed tanks and methanol addition at several points along the reactor would reduce the system's methanol requirements. Attempts to reduce the methanol requirement by utilizing waste activated sludge did not provide substantial improvement in system performance. Raw wastewater, primary effluent, and primary solids were eliminated from consideration since they also add organic and ammonia nitrogen as well as grease, rags and floatables.

In an open reactor, the objective is to mix the solids just fast enough to keep them in suspension. Figure 8 shows the influence of mixing upon solids concentration and apparent dissolved oxygen depletion rate. In the seven-day studies, the pilot plant's horizontal flocculators were operated at 2 1/4 rpm which corresponds to an approximate tip speed of 0.75 ft/sec (0.24 m/sec) and velocity gradient of 5 to 8 ft/sec/ft. Enough mixing variability should be provided to remove any accumulated solids from the tank's liquid surface. The preferred design may be one which completely sealed the tank, with a slight vacuum provided to remove the off-gases and prevent oxygen transfer at the air/liquid interface. Although this would increase capital costs it may result in a substantially reduced methanol requirement for denitrification. Sealed tanks would allow off-gas recirculation and mixing.

Preceding the pilot plant's denitrification tank is a flash mixer which was provided to intimately mix the methanol, nitrified effluent and return sludge. The highly soluble nature of methanol makes this process step unnecessary and in-line mixing should be completely satisfactory. The aeration channel following the denitrification reactor was provided to furnish effluent dissolved oxygen, remove any remaining carbonaceous oxygen demand, and to strip off any adhered nitrogen gas bubbles from the sludge floc. Experience has shown that sludge floc disintegration occurs at the high aeration rates required in a short detention time to meet an effluent requirement of 5 mg/l dissolved oxygen. Post aeration after solids separation is recommended as the means of meeting effluent dissolved oxygen requirements. Profiles through the denitrification system have shown only minimal quantities of soluble biodegradable carbon left from a three sludge system with proper methanol dosage. Operation with and without the channel in service

FIGURE 8 - PHYSICAL PERFORMANCE OF THE DENITRIFICATION SYSTEM
(no substrate addition)



has shown that some means of agitation is necessary to strip off the nitrogen bubbles from the mixed liquor solids. This can be done by greater velocity gradients within the denitrification system, by passing the solids over a final weir, or by a very brief period of gentle air agitation.

FUTURE STUDIES

The final year of pilot plant operation is oriented to obtaining detailed design and operational criteria for a three sludge, combined biological and chemical, nitrogen and phosphorus removal system. Seasonal, long-term evaluation with diurnal flows will be investigated. Liquid alum for phosphorus removal and a tri-media filter for final effluent solids control will be incorporated.

CONCLUSIONS

The three sludge system, although slightly more expensive than the other activated sludge systems investigated, offers the most dependable, consistent performance for achieving nitrification. Nitrification can be provided at a capital cost within plus or minus ten percent of the cost of conventional activated sludge treatment. Alkalinity depletion due to nitrification will be less than that theoretically predicted but in low alkaline wastewaters it may be of sufficient magnitude to necessitate the addition of an external source of alkalinity for pH control.

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